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SIMULATION OF THE MASSIVE FRACTIONATION OBSERVED IN CO PHOTODISSOCIATION EXPERIMENTS

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Introduction: The observation of massive fractionation (~10,000 ‰) in CO_2 produced in laboratory CO photolysis experiments [1] provides a superb illustration of the process of self-shielding. Self-shielding results from the saturation of CO isotopologue absorption lines, and yields an abundance-dependent fractionation upon dissociation. Because $^{12}C^{16}O$ is ~500 times more abundant than $^{12}C^{18}O$, saturation of $^{12}C^{16}O$ lines occurs at much lower gas column densities than for the rare isotopologues, creating a region of ^{17}O and ^{18}O-enriched O atoms. CO self-shielding is essential to understanding the distribution of oxygen isotopes in the solar system [2],[3],[4]. For the experiments performed in [1] the typical column densities were ~10^{18} cm^{-2}, implying $^{12}C^{16}O$ optical depths >1000 [5]. Thus, self-shielding was unavoidable in these experiments. In order to elucidate the origin of the large fractionations measured in [1], we have performed detailed modeling of the photolysis of the CO E(0) – X(0), E(1) – X(0), and C(1) – X(0) bands at 107.6, 105.17, and 106.3 nm, respectively. To the cross sections computed in [6] we have included the perturbation of the E(1) state by the k(6) triplet state using the formalism of [7].

Results: For simulation of the experiments at 105.17 nm, the model $\delta^xO'(CO_2)$ values are ~6,000–12,000 ‰ (comparable to measured values), but have a δ^{17}/δ^{18} slope ~1.05, lower than the measured value of 1.3. $\delta^xO'(CO_2)$ decrease with CO column density and become negligible when optical depth is <<1, as expected for a self-shielding effect. Low optical depth experiments are needed to confirm this result. The δ^{17}/δ^{18} slope can be accounted for by a 30% stronger band oscillator strength for $^{12}C^{17}O$ versus $^{12}C^{18}O$. However, we do not expect such large isotopic variation in band oscillator strengths, and doubt that this is a satisfactory explanation.

Simulation results [6] for the synchrotron beam at 107.61 nm (E(0) band) show that a slope ~1.4, comparable to the measured values, occurs at the highest column densities (as observed), but is not present at lower densities. It is important to note that self-shielding does occur in this band, contrary to the claims of [1]. The non-unity δ^{17}/δ^{18} slope arises from the pattern of closely overlapping lines among the isotopologue spectra.

Conclusions: The key results here are that massive fractionation is expected from self-shielding alone, and that the fractionation depends on wavelength. The δ^{17}/δ^{18} slope associated with CO photolysis must be determined from the summation over all CO bands for comparison with the CAI line (0.95–1.0).

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DISCOVERY OF A NEW PHOSPHIDE MINERAL, MONIPITE (MONIP), IN AN ALLENDE TYPE B1 CAI

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Introduction: During our nano-mineralogy investigation of the Allende meteorite, a new phosphide mineral, monipite (MoNiP), was discovered in a Type B1 Ca-, Al-rich inclusion (CAI). Monipite, the Mo-, Ni-dominant analog of barringerite (Fe_2P), is named for the composition. It is probably a secondary product of the oxidation of Mo-phosphides and/or P-rich alloys and reflects conditions during the alteration of CAIs. The mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2007-033). We report here the first occurrence of monipite in nature and a new phase for CAIs.

Occurrence, Chemistry, Crystallography: Monipite occurs as one irregular grain, 1.3 × 2.0 m in size, in the melilite-rich mantle of a type B1 CAI (section USNM 7554). With an empirical formula based on election probe microanalysis of $(Mo_{0.84}Fe_{0.06}Co_{0.04}Rh_{0.03})_{0.97}(Ni_{0.89}\ Ru_{0.09})_{0.98}P$. The monipite grain is in contact with apatite, tugarinovite (MoO_2), and a Ru-Mo-Ni metal grain; the surrounding phases include apatite, V-rich magnetite, kamiokite ($Fe_2Mo_3O_8$), tugarinovite (MoO_2), a Mo-Fe oxide with Mo/Fe ~2, and Nb-rich oxide ($(Nb,V,Fe)O_2$). This assemblage is bounded by Ni_2Fe on one side and coarse-grained clinopyroxene + spinel on the other. To our knowledge, monipite is the first known occurrence of a phosphide in an Allende CAI; this is also the first reported meteoritic occurrence of kamiokite, tugarinovite, the Mo-Fe oxide with Mo/Fe ~2, and the Nb-rich oxide. Electron backscatter diffraction patterns of monipite were matched against the structures of known synthetic phases in the Mo-Ni-P system. The best fit was achieved using the $P\bar{6}2m$ MoNiP structure [1], with a = 5.861 Å, c = 3.704 Å, V= 110.19 Å^3, Z = 3. The calculated density is 8.27 g/cm^3.

Origin and Significance: Monipite, together with Ru-Mo-Ni alloy and kamiokite, are surrounded by a ~12 μm diameter rosette composed of apatite, Nb-rich oxide, a Mo-Fe oxide with Mo/Fe ~2, V-bearing magnetite, kamiokite, and tugarinovite. The phase distribution is asymmetric with Nb-rich oxide restricted to the pyroxene-spinel bounded side of the assemblage and Mo ± Fe oxides concentrated towards the Ni_2Fe alloy side. A simple scenario for the formation of monipite is that a precursor in melilite consisted of a Mo + P-rich alloy ± phosphide, which was oxidized during alteration to produce the observed aureole of oxide and phosphate alteration phases. Ca, Mo, Fe and, possibly, Ni were mobile during metasomatism and, in particular, the aureole supported large chemical potential gradients in Mo over a few μm. It seems likely that monipite would have been destroyed given sufficient time and access to the altering medium. Nevertheless, monipite and its escorts hold new information on the processes to which Allende CAIs were subjected after their formation and, together with other new Allende minerals [2–4], provide new insight into the formation and evolution of the early solar system.

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